

## **Enhancing the Flame Retardancy of UV Curable Polyurethane Acrylate Coated Films with Alumina Trihydrate Filling**

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### **Abstract**

In this study, the flame retardancy of ultra violet (UV) curable polyurethane acrylate (PU) coated films were enhanced. For this aim, alumina trihydrate (ATH) filling material was mixed with the pastes including a photoinitiator and a UV curable PU. ATH filling ratio was precisely adjusted to obtain a uniform coating. The coated films were cured with a UV curing system equipped with gallium (Ga) and mercury (Hg) lamps. The chemical changes and the curing degree of the UV cured films were examined by a Fourier Transform Infrared Spectrum (FTIR) and a pendulum hardness tester. The thermal properties of the UV cured films were evaluated using a Differential Scanning Calorimeter (DSC). Moreover, vertical flammability and limiting oxygen index (LOI) measurements were conducted in order to determine the burning behavior of the UV cured films. The successful curing of the films was evidenced by means of FTIR results. The addition of ATH slightly increased the hardness values of the films. DSC results showed that ATH addition not only increased the enthalpy values but also enhanced the flame retardant property of the coated films and maximum LOI was achieved as 31.5%.

**Keywords:** Flame retardancy, Polyurethane acrylate, Coating, UV curable, Aluminum trihydrate, LOI

### **Ultraviyole (UV) Işıma ile Kürlenebilen Poliüretan Akrilat Kaplama Filmlerin Alev Geciktirici Özelliğinin Alümina Trihidrat Dolgu Malzemesi Kullanılarak İyileştirilmesi**

### **Öz**

Bu çalışmada, ultraviyole (UV) ile kürlenebilen poliüretan akrilat (PU) kaplama filmlerin alev geciktirici özelliği iyileştirilmiştir. Bu amaçla alümina trihidrat (ATH) dolgu malzemesi, bir fotobaşlatıcı ve UV ile kürlenebilen PU içeren pat ile karıştırılmıştır. ATH dolgu oranı düzgün bir kaplama elde edilecek şekilde hassas olarak ayarlanmıştır. Kaplanmış filmler galyum (Ga) ve civa (Hg) lambaları ile donatılmış bir UV kürlenme sistemi ile kürlenmiştir. UV ile kürlenmiş filmlerin kimyasal değişimleri ve kürlenme derecesi Fourier Transform Infrared Spektroskopisi (FTIR) ve pendulum sertlik test cihazı ile incelenmiştir. UV ile kürlenmiş filmlerin termal özellikleri Diferansiyel Taramalı Kalorimetre (DSC) kullanılarak değerlendirilmiştir. Ayrıca, UV ile kürlenmiş filmlerin yanma davranışını belirlemek için dikey yanma ve sınırlı oksijen indeksi (LOI) ölçümleri yapılmıştır. Filmlerin başarılı bir şekilde polimerleştirilmesi FTIR

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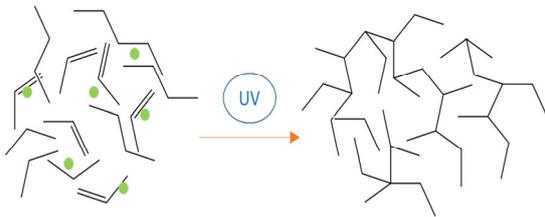
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sonuçları ile kanıtlanmıştır. ATH'nin eklenmesi, filmlerin sertlik değerlerinin az bir miktar artmasına sebep olmuştur. DSC sonuçları, ATH ilavesinin sadece entalpi değerlerini artırmakla kalmayıp, aynı zamanda kaplanmış filmlerin alev geciktirici özelliğini de artırdığını göstermiştir ve maksimum LOI değeri % 31,5 olarak elde edilmiştir.

**Anahtar Kelimeler:** Alev geciktirici, Poliüretan akrilat, Kaplama, UV (ultraviyole) kürleme, Alümina trihidrat (ATH), Sınırlı oksijen indeksi (LOI)

## 1. INTRODUCTION

UV curable coatings are gaining importance compared to the solvent based thermal curable coatings due to environmental concerns, health and safety risks [1]. Since thermal curable coatings are odorous and generate VOC emission, UV curable coatings have been produced to eliminate these disadvantages [2]. In UV curable coatings, a polymerization reaction of an unsaturated resin induced by incident radiation is followed by a curing reaction which is carried under room temperature within few seconds, transforming the liquid polymer into solid (Figure 1) [3].



**Figure 1.** Schematic description of crosslinking of WPU by UV curing

Most of the UV curable formulations include photoinitiators, which are responsible for radical production, together with the reactive resin. The polymerization of the reactive resins occurs generally through polymerizable double bonds. The polymerizations, which are initiated with the photoinitiators, occur in three stages, initiation, propagation and termination. The applied UV energy may split the of C–C and C–H bonds. However, since the common monomers possess low absorbance and insufficient cleavage efficiency, the amount of initiating radicals produced by the monomers after UV exposure are also insufficient. Therefore, photoinitiators are usually included in the formulations [4].

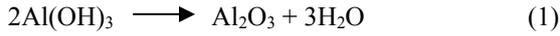
Polyurethane-acrylates (PUA) have been used as coatings, adhesives, fibers, foams, and thermoplastic elastomers [2,5,6].

UV curable coatings find applications in decoration and protection of upholstery and plastic products [3], due to their good properties of flexibility, durability, impact and tensile strength, scratch and abrasion resistance, and weather stability [7].

Burning mechanism can be explained in five basic steps which are; heating, decomposition, ignition, combustion and propagation [8-10]. Combustion is a complex physical and chemical process, and defined by the combination of gas-phase and the condensed-phase actions. Several systematic principles were presented to understand the mechanism, however, it is not possible to identify one dominant mechanism for combustion which have a key role in the flame retardancy [11]. Usage of flame retardants reduces the combustion of the material and limited their smoke or toxic fume [5]. Selection of a flame retardant has a crucial role in the development of FR applications. Well-known way to reduce flammability of the polymeric composite is introducing micro/nano flame retardants into the materials [9]. As inorganic compounds; aluminum trihydrate or aluminum hydroxide (ATH) and magnesium hydroxide were mainly studied metallic hydroxides employed to decrease the polymer's surface temperature and retard the pyrolysis of the polymer due to their endothermic decomposition nature [8,12,13]. According to literature, a coating using a metal oxide can act as an insulating protective layer during combustion [12,14,15].

Flame resistance by aluminum trihydrate, and magnesium hydroxide is obtained by loading a very high portion, i.e. more than 40% wt. %, of the filler materials within the polymer matrix [16,17]. ATH

is a low cost flame retardant active filler used to enhance the flame resistance of the structures [8], [18] which is generally used at higher loading ratios such as 60 weight-% inside the composite [17]. ATH starts decomposition at around 220 °C via endothermic reactions and decomposed as [10]; (Equation 1)



Similar to the other organic materials, Polyurethanes (PUs) are commonly used polymers while they have an important drawback by their flammability [17,19].

It is a major challenge in scientific area to improve fire resistance of PU-based coatings by incorporation of the appropriate fire retardants [20]. In the literature, ATH filler was studied as a fire retardant inside the PU matrix along with mica [5]. However, studies on the use of ATH filling in PU coatings, which can be cured with UV, are limited [4,21-23].

To the best of the authors' knowledge, two studies in the literature examine the effect of incorporation of ATH filler in a UV curable polyurethane acrylate system. Dando *et al.* characterized the effects of different amounts of ATH on the UV transparency, enthalpy of cure, and cure kinetics of UV-curable inks [22].

Parker *et al.* used ATH as an extender in UV-cured PU films, and compared the UV transparency of ATH and silica-filled films. It was reported that, ATH-filled films exhibited higher degrees of cure than the silica-filled system, since ATH did not interfere with the transmittance of UV light [23]. However, the effect of incorporation of ATH filler as a flame retardant in a UV curable polyurethane acrylate film has not been examined in the previous studies. Thus, in the current study, ATH filler was firstly used to improve the flame resistancy performance of a UV curable PU coating and optimal coating and curing conditions were investigated to achieve a uniform coating layer. Flame resistancy of the coating was examined by vertical flammability and limiting oxygen index (LOI) measurements.

## 2. EXPERIMENTAL

### 2.1. Materials and Methods

Aromatic urethane acrylate based Laromer 9065 was purchased from BASF® and used as received. ATH was purchased from Mikron'S (with a Mw of 78.00) and used in powder form as received and Irgacure® 184 as photoinitiator was delivered from Ciba Specialty Chemical and used without any further purification.

In the literature, UV curable lacquers comprised 1-8% photoinitiator which was adjusted according to the application process and coating requirements [4]. In this study, Irgacure® 184 was used at a ratio of 3.5%. A mechanical mixer (Yokes) was used to obtain a homogeneous mixture of all chemicals. As previously reported, higher mixing speeds are required for a well dispersion of all compounds [10,16,24]. The initial mixture (comprising Laromer/Irgacure/ATH) was first combined together in the beaker and was then mixed at 120 rpm for 5 minutes and subsequently at 3000 rpm for 5 min, at room temperature. A film coating apparatus was used to spread the coating paste on a glass plate to produce the films with 120 µm thickness. Curing process was applied at room temperature in a UV curing machine equipped with gallium (Ga: 380 Volt, λmax: 400-450 nm) and mercury (Hg: 220 Volt, λmax: 300-365 nm) lamps and a conveyor belt with an adjustable speed. The speed of belt was set to 10m/min and applied energy was measured as 1191 mJ/cm<sup>2</sup> with a UV-Integrator Type D radiometer from Beltron GmbH (Germany).

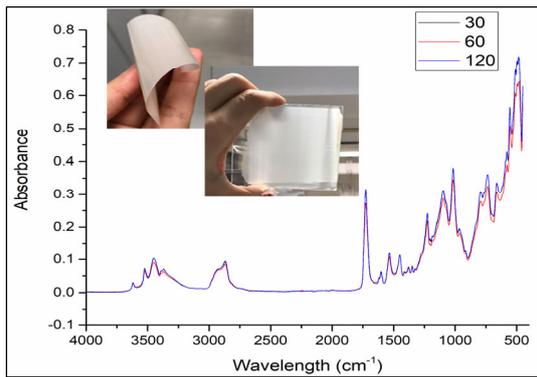
FTIR (Perkin Elmer) was used to record characteristic peaks of the structure before and after UV curing. Differential Scanning Calorimetry (Perkin Elmer, Q4000) was used for thermal analyses. The König hardness of polymeric films was evaluated with Byk Pendulum Hardness Tester according to the ASTM D4366 and the hardness value was reported in seconds (s). Standard Test Method for Flame Resistancy of Textiles (Vertical Test) ASTM, D6413/D6413M-15 standard was followed for the burning tests. Moreover, the LOI

values of the UV cured films were measured according to the BS 4589-2 standard.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. FTIR Spectrophotometer Analysis

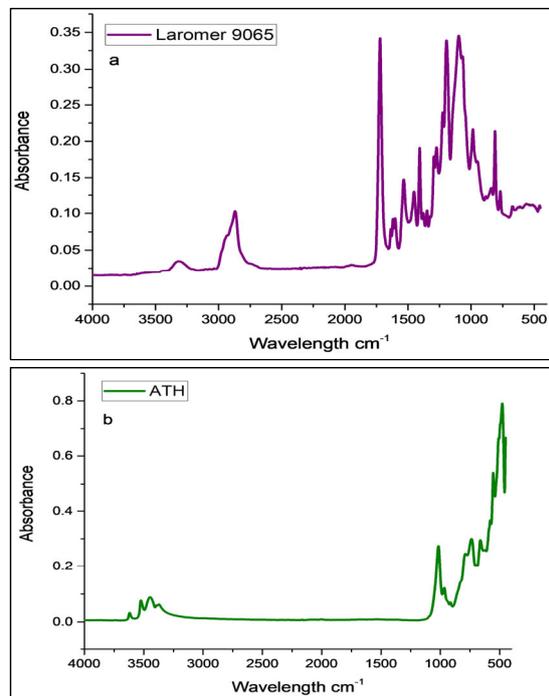
Prepared and cured PU films containing ATH in powder form were investigated with FTIR spectrometer to analyze the chemical changes in structure through curing and compare the difference for changing ATH amounts (PU/ATH; 100/100, 100/120, 100/140, 100/160). As seen in the photographical images of the films in Figure 2, the produced plastic films are flexible and visually semi opaque. Characteristic peaks of PU and ATH recorded by FTIR spectrometer were presented in Figure 3.



**Figure 2.** FTIR spectra of different coating thicknesses (30, 60 and 120  $\mu\text{m}$ ) of the PU/100 ATH film and inset figure is photograph image of the flexible and homogenous coating of PU/ATH film

At  $1720\text{ cm}^{-1}$  C=O stretching bond can be attributed to the urethane [25,26]. Amide-I is located to that peak and intensity change of the peak represents the changing amount of carbonyl H- bonds [27,28]. After UV curing, C=C stretching vibration of vinyl group which is around  $1635\text{ cm}^{-1}$  and the peak around  $810\text{ cm}^{-1}$  (CH bending), which come from the PU, decreased (Figure 4). Peak at  $1635\text{ cm}^{-1}$  reflecting the C=C stretching of acrylate which have been incorporated in the polyurethane chain [2], and peak at  $810\text{ cm}^{-1}$  reflecting the CH peak were

recorded for PU. However, after UV curing, these peaks could not be detected for the UV cured polymers. The acrylate double bonds which are necessary to crosslink the polymer disappeared after the polymerization [29]. During the polymerization of PU, CH bonds start to break for the conversion of the polymeric structure. After the curing process, disappearance of the CH on the FTIR spectra proved that the curing was successfully achieved for the selected ATH filling ratios and shown in Figure 4.



**Figure 3.** (a) FTIR spectra of Laromer 9065 as WPU, (b) FTIR spectra of ATH

Absorption peak around  $2865\text{ cm}^{-1}$  represents the  $\text{CH}_2$  and  $\text{CH}_3$  bands and peak around  $3360\text{ cm}^{-1}$  represents the NH, hydrogen bonding, which are typical for polyurethanes [2].

ATH has hydroxide groups and their peaks appear at around  $3500\text{ cm}^{-1}$  [30]. Figure 5 represents the spectra of all of the studied PU samples with and without ATH. ATH addition can be easily followed with the peaks located around  $3500\text{ cm}^{-1}$  originating due to OH units of ATH.

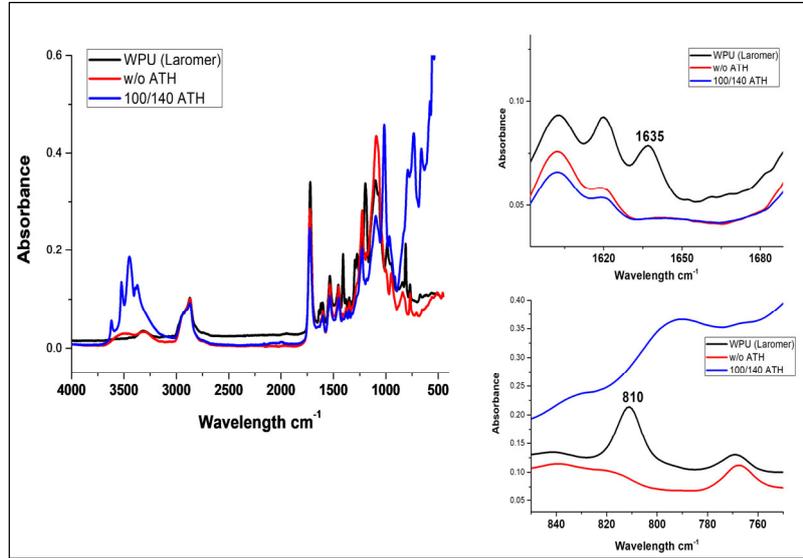


Figure 4. FTIR results of WPU, PU w/o ATH and PU/ATH

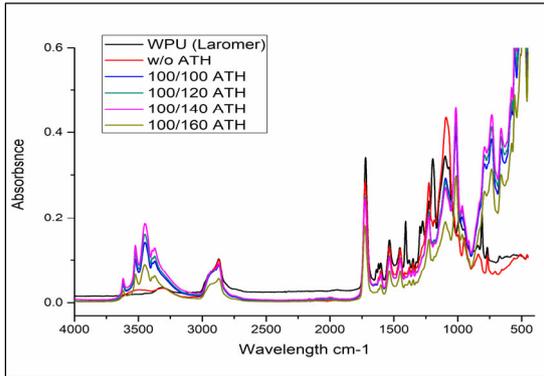


Figure 5. FTIR Spectra of different WPU/ATH ratios and WPU after curing

### 3.2. Hardness Analysis

König hardness values of the ATH filled coatings were measured with a pendulum hardness tester. The results showed that, the hardness values of the coating slightly increased with the addition of ATH (Table 1). It was reported that the incorporation of ATH into coatings resulted in an increase of the hardness value of the coating [31]. It is expected that, the addition of a filler into a UV curable PUA resin would result in a lower photopolymerization due to the screen effect of particles, reducing the penetration of UV light [32,33], which in turn may

reduce the hardness value of the film. However, in case of ATH filled films, the hardness values were found similar among each other, and higher than that of clear films. This can be attributed to the low UV absorption of ATH [34].

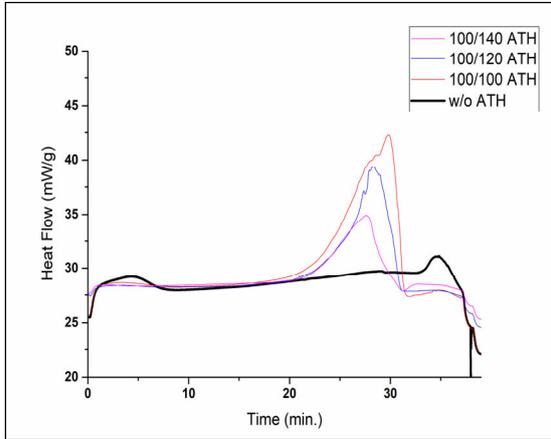
Table 1. Koenig Hardness results for coatings

Sample	Koenig (s)
w/o ATH	26.8±1.05
100 ATH	30.8±0.00
120 ATH	30.8±0.00
140 ATH	32.7±1.69
160 ATH	30.8±1.98

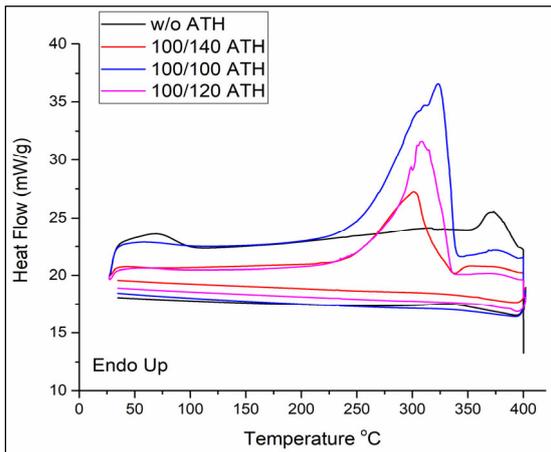
Hence, ATH can be incorporated in a UV curable PU coating without any significant effect on curing levels. Moreover, ATH addition slightly increased the hardness values of the cured films. Inorganic compounds can act as fillers to improve certain mechanical properties of polymers; moreover, inorganic fillers assist to reduce their cost [5,35].

### 3.3. Thermal Analysis (DSC) and Burning Behavior

The results of DSC thermal analysis of PU coatings without and with different ATH filling ratios after curing were given in Figure 6a and Figure 6b.



**Figure 6a.** DSC plot of PU/ATH coatings, heat flow vs. time



**Figure 6b.** DSC plot of PU/ATH coatings, heat flow vs. temperature

The enthalpies of decomposition measured under nitrogen environment were given in Table 2. Enthalpy values were improved with the increased filling amount of ATH. Figure 6a shows the heat flow value change versus time and according to the results, reaction started earlier for ATH containing PU samples compared to samples without ATH. The decomposition reaction of ATH is endothermic and releases H<sub>2</sub>O [24,36] and endothermic peak was seen in Figure 6b. As can be seen in Figure 6b, above 250 °C, ATH act as a thermal barrier [36] compared to polymer without ATH. Since ATH forms an insulating protective layer on the surface

[37], its DSC curve is stable. Moreover, DSC results showed increased heat capacity for the films with increased ATH amount. In agreement with the previous studies T<sub>g</sub> of PU was measured at around 53°C [38-40] however the addition of ATH filler to PU eliminated the T<sub>g</sub> value.

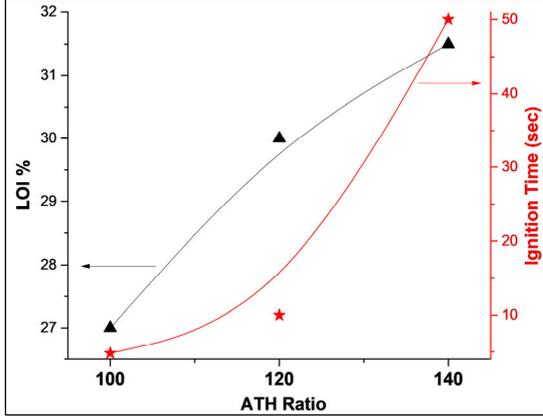
**Table 2.** Total enthalpy values of PU/ATH coatings

Sample	Peak Temperature (°C)	ΔH (J/g)	Burning Time (sec)
w/o ATH	373.00	40.49	1.0
100	323.58	446.08	4.8
120	308.70	473.83	10.0
140	301.42	476.55	50.0
160	-	-	56.0

The films with and without ATH were exposed to the flame and their burning behaviors were evaluated. The flame application times (the time for which the ignition flame was applied to the samples) are shown in Table 2. The flame application was halted after ignition of the samples. Samples released a black smoke while burning and there was not any dripping observed after removal of ignition source. Burning time was dramatically improved for PU film after addition of ATH. As it is reported elsewhere, flame retardancy characteristics of polymers can be enhanced with increased amount of ATH [41,42]. However, although ATH filling retards the burning time, in order to obtain a uniform coating, ATH amount should be well adjusted.

Flame retardancy performance of the films were also investigated with LOI values which provide a percentage range and a comparison between the samples. Figure 7 shows the effect of ATH ratio on LOI and ignition time. ATH addition had a positive effect on the flame retardancy of the films. LOI values changed between 27 to 31.5% as in the range reported in previous studies on ATH containing polymeric materials [43,44]. In the literature [27] polyurethane acrylates used for UV curable coatings showed the maximum LOI value of 27%.

On the other hand, in our study, without damaging the homogeneity of the film 100/140 ratio gives the excellent LOI result of 31.5%.



**Figure 7.** Comparison of LOI% values and ignition time of samples according to their ATH content

#### 4. CONCLUSION

In this study, ATH containing UV curable polyurethane acrylate coatings were successfully developed to enhance the flame retardancy. Hardness values were slightly increased with the increase of ATH ratio in the cured film. Different ATH filling ratios were studied and it was found that above 100/140 feeding ratio, the mixing performance diminishes leading to a nonhomogeneous film. Thus, 100/140 ATH filling ratio was selected as an optimum to provide the homogeneity of the coating.

DSC results showed the positive effect of ATH addition in the polymer matrix resulting in increased enthalpy. Burning behavior of the films in a horizontal position showed that ATH addition retarded the burning of the film. When the burning behavior of polyurethane acrylate coating without ATH filling was compared with the ATH filled coating, 100/140 ratio gives a 50 times more improvement on the burning time. Whereas maximum 21% oxygen is needed to combustion on the air, in this study satisfactory LOI (31.5%) and ignition time values were achieved for the 100/140 ratio coating. Thus, the incorporation of ATH filling

was found to be promising for the flame retardant enhancement of UV curable PU coatings.

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